

10 / 511008
PCT AU03/00417



REC'D 25 APR 2003

WIPO PCT

12 OCT 2004

**PRIORITY
DOCUMENT**

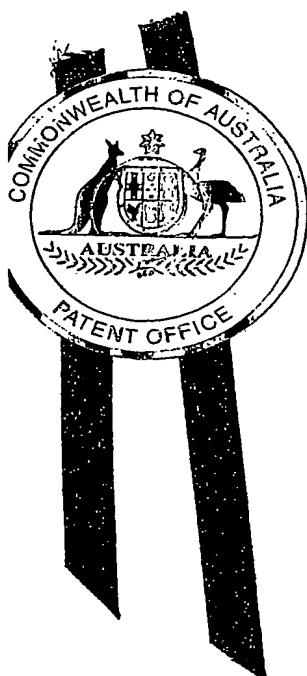
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Patent Office
Canberra

I, JONNE YABSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PS 1568 for a patent by BERTSHELL PTY LTD and MACQUARIE VETERINARY SUPPLIES PTY LTD as filed on 05 April 2002.

WITNESS my hand this
Fifteenth day of April 2003

JONNE YABSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES



ORIGINAL

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

Process and Apparatus for Use in Preparing an Aqueous Magnesium Bicarbonate Solution

Names and Addresses of Applicants:

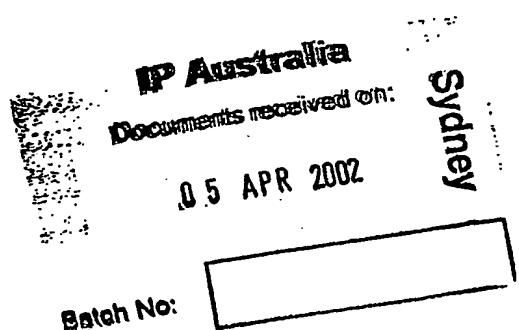
Bertshell Pty Ltd, an Australian Company (ACN 000 470 066), of 45-47 Alexander Avenue, Taren Point, New South Wales, 2229, Australia

Macquarie Veterinary Supplies Pty Ltd, An Australian Company, ACN 000 768 132, of 4 Charlotte Street, Red Hill, Australian Capital Territory, 2603, Australia

Names of Inventors:

Arthur Shelley and Dennis Shelley and Russell John Beckett

This invention is best described in the following statement:



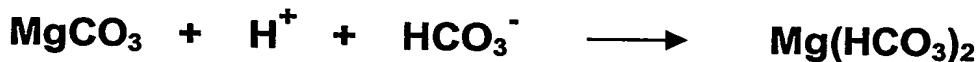
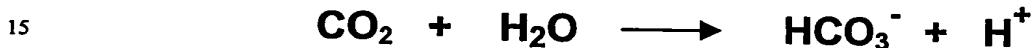
PROCESS AND APPARATUS FOR USE IN PREPARING AN AQUEOUS MAGNESIUM BICARBONATE SOLUTION

Technical Field

The present invention relates to the preparation of an aqueous magnesium bicarbonate solution. More particularly, the invention relates to a process and an apparatus for use in bottling an aqueous magnesium bicarbonate solution.

Background of the Invention

In Patent Application PCT/AU/98/00168 and in Australia Patent No 735 435, a process for the manufacture of a mildly alkaline magnesium bicarbonate solution from magnesium carbonate powder dispersed in water, using carbon dioxide absorbed into the water from the gaseous state, is described. In that process, dissolved carbon dioxide reacts with the magnesium carbonate either while it is still in its solid form as a suspension in water or upon dissolution thereof in water, to form magnesium bicarbonate:



The time required for the above chemical reactions to run to completion to ensure the clarity or clearness of the final solution was stated in Patent Application PCT/AU/98/00168 and in Australia Patent No 735435 to be not less than 6 hours, typically from 6 hours to seven days, more typically from 24 hours to 72 hours.

It has been found by the applicant to be undesirable to bottle magnesium bicarbonate too early, particularly if the turbidity caused by the remaining magnesium carbonate powder is too high, because the undissolved magnesium carbonate does not dissolve easily after the solution has been bottled. This lack of dissolution occurs even when magnesium carbonate powder is reduced to very small (less than 1 micron) particle sizes.

The long reaction time of the aforementioned process is thought to be due to the inherent kinetics of the chemistry involved and has been found to be disadvantageous for purposes of the commercial bottling of specific magnesium bicarbonate solutions, in view of the adverse effect it has on processing time and hence plant capacity.

There accordingly exists a need for a process for the manufacture of a magnesium bicarbonate containing solution that has a decreased reaction time under temperature conditions which are favourable for the rapid dissolution of carbon dioxide in water.

There also exists a need for a process for the bottling of a magnesium bicarbonate containing solution that will be substantially clear or that will become substantially clear within a relatively short period after bottling, which period may be from one to eight hours after bottling.

Object of the Invention

It is an object of the present invention to overcome or substantially ameliorate at least one of the above-mentioned disadvantages and/or to address at least one of the aforementioned needs.

Summary of the Invention

According to a first aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate at a pH, after reaction of the said species with the magnesium carbonate, falling within a range of from about 8,0 to about 8,8; and
- controlling the pH of the said solution within the said range until substantially all of the said magnesium carbonate has been converted to dissolved magnesium bicarbonate.

The pH may be controlled by decreasing or increasing the pH of the aqueous suspension of magnesium carbonate and of the resulting solution by dissolving in the suspension a larger or a smaller amount of carbon dioxide. Alternatively, the pH may be controlled by increasing or decreasing the amount of magnesium carbonate introduced into the suspension. As another alternative, the pH may be controlled by introducing into the solution protons or a substance which has an effect on the pH.

According to a second aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate at a pH, after reaction of the said species with the magnesium carbonate, falling within a range of from about 8,0 to about 8,8; and
- agitating the suspension so as to keep in suspension a major portion of the magnesium carbonate until substantially all of the said magnesium carbonate has been converted to dissolved magnesium bicarbonate.

The major portion of the magnesium carbonate may be any proportion from about 5 30% to about 100% of the magnesium carbonate forming part of the said suspension.

The method according to the second aspect of the invention may conveniently also include a step in which the pH is controlled. This may be achieved by either decreasing or increasing the pH of the aqueous suspension of magnesium carbonate and of the resulting solution by dissolving in the suspension a larger or a smaller amount of carbon dioxide.

15 Alternatively, the pH may be controlled by increasing or decreasing the amount of magnesium carbonate introduced into the suspension. As another alternative, the pH may be controlled by introducing into the solution protons or a substance which has an effect on the pH.

20 The pH of the aqueous suspension of magnesium carbonate may advantageously be controlled to be above about 8, ideally between about 8,2 and about 8,6.

The method according to these aspects of the invention may include the step of controlling the pressure at an absolute pressure of from about 50 kPa to about 500 kPa.

25 The aqueous suspension of magnesium carbonate preferably contains from about 50 mg to about 200 milligrams of magnesium per litre of water, more particularly from about 90 mg per litre to 150 mg per litre, even more particularly from about 100 mg per litre to about 140 mg per litre. The aqueous solution of magnesium bicarbonate obtained may have a concentration of bicarbonate anions from about 200 mg per litre to about 1000 mg per litre, more particularly from about 400 mg per litre to 800 mg per litre, even more particularly from about 500 mg per litre to 700 mg per litre.

30 By carefully following the teachings of the present invention, the aqueous solution of magnesium bicarbonate may be produced in commercial quantities in less than about 6 hours.

The species resulting from the dissolution of carbon dioxide in water may include protons and bicarbonate ions. Alternatively or additionally, it may include carbonic acid.

The magnesium carbonate is preferably contacted with a stoichiometric quantity of species resulting from the dissolution of carbon dioxide in water, or with a quantity of such species which exceeds a stoichiometric quantity by from about 0% to about 20%, preferably by no more than about 10%, more preferably, by no more than about 1% to about 5%.

The temperature of the aqueous suspension of magnesium carbonate may also be controlled. The temperature may be controlled between about 0°C and about 25°C.

It is to be understood that at lower temperatures, the rate of dissolution of carbon dioxide in water is faster than at higher temperatures. However, the rate of the reaction of magnesium carbonate with the species resulting from the dissolution of carbon dioxide in water, to form magnesium bicarbonate, is lower at lower temperature. Thus, the temperature of the aqueous suspension of magnesium carbonate water may be controlled at such a level as to achieve a desired absorption of carbon dioxide into the suspension consistent with a desired rate of reaction between magnesium carbonate and the species formed as a result of the dissolution of carbon dioxide in the suspension. Preferably, the temperature is maintained below about 25°C in the range between about 1°C and about 20°C, more preferably below about 16°C in the range between about 5°C and about 16°C, even more preferably in the range between about 10°C and about 16°C, ideally in the range of from about 12°C to about 16°C., even more ideally between about 12°C and about 15°C.

The contacting step of either the first or the second aspect of the invention may be conducted either continuously or batchwise.

The method in accordance with the first and second aspects of the invention may conveniently also include the additional step of bottling the said aqueous solution of magnesium bicarbonate, preferably under an atmosphere containing carbon dioxide, preferably at an absolute pressure of from about 50 kPa to about 500 kPa. Alternatively, the solution may be bottled under air or nitrogen, at a pressure from about 50kPa to about 500kPa.

The bottling step is preferably carried out when the magnesium bicarbonate solution is clear, or, in order to reduce processing time, whilst the turbidity of the magnesium bicarbonate solution is no more than a slight haze and the pH falls within the range of about pH 7.0 to pH 9.0, ideally from about pH 7.8 to pH 8.8, more ideally from about pH 8.0 to pH 8.6. It has been found that if the turbidity is low enough, the solution will clear up after bottling if the pH falls within this range, but when the turbidity is too high, the

solution either does not clear up after bottling or the end pH, after complete reaction of said species with the magnesium carbonate, is too high. If the pH value exceeds pH 9.0, the taste of the magnesium bicarbonate solution becomes unacceptable as it tends to be too caustic. Above pH 9.0 carbonate floccules may reappear in the solution. If the pH 5 value falls below pH 7.0, the medical value of the magnesium bicarbonate solution is largely negated.

In order to prevent the presence of unwanted foreign matter in the magnesium bicarbonate solution, the method according to the first and second aspects of the invention may include the step of passing any one or more of the suspension, the solution and the 10 water to be used for the preparation of the aqueous magnesium carbonate suspension through a filter having a maximum pore size of about 10 microns, preferably having a maximum pore size of about 5 microns, more preferably having a maximum pore size of about 2 microns.

According to a third aspect of the present invention, there is provided an apparatus 15 suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:

- means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate; and
- means for controlling the pH of the solution between about 7 and about 9 by adjusting 20 the amount of at least one of the said species and the said powdered magnesium carbonate that is contacted with the other.

The apparatus according to the third aspect of the invention may also comprise means for keeping in suspension a major portion of said powdered magnesium carbonate.

According to a fourth aspect of the present invention, there is provided an apparatus 25 suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:

- means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate; and
- means for keeping in suspension a major portion of said powdered magnesium 30 carbonate until substantially all of the suspended magnesium carbonate has been converted to dissolved magnesium bicarbonate.

The apparatus according to the fourth aspect of the invention may also comprise means for controlling the pH of the solution between about 7 and about 9. This may be

achieved by means adapted to adjust the amount of at least one of the said species and the said powdered magnesium carbonate that is present in the apparatus.

The apparatus according to the third and fourth aspects of the invention may also comprise means for bottling the solution of magnesium bicarbonate.

5 The means for contacting may comprise means, such as a tank of sufficient size, for containing the suspension and the species resulting from the dissolution of carbon dioxide in water. In a batch process, a tank large enough to contain all of the magnesium bicarbonate solution required for a production run in which a certain number of bottles are filled with the solution, may be provided. In the case of a continuous process, a
10 smaller container may be sufficient for the contacting step, although a suitable reactor and/or clarifier or other similar but suitable pieces of equipment may be provided to ensure that the reaction between the magnesium carbonate and the said species is permitted to run to substantial completion.

15 The means for contacting with magnesium carbonate the species resulting from the dissolution of carbon dioxide in water may also comprise means for dissolving carbon dioxide in the water or in the said suspension so as to form a solution containing the said species.

20 The means for dissolving carbon dioxide may comprise a sparger comprising a fine mesh such as a stocking like mesh, or another suitable device capable of breaking up the carbon dioxide into small bubbles. The sparger may conveniently comprise a porous separation means adapted to separate pressurised carbon dioxide from water into which the carbon dioxide is to be dissolved, the pores of the separation means extending from a gas side thereof to a water side thereof, in use, and to break the carbon dioxide up into a plurality of small bubbles, for increasing the intimacy of contact between the carbon dioxide and the water.
25

30 The means for dissolving carbon dioxide may comprise, in addition to or as an alternative to the aforementioned sparger means, a tube and a helical baffle locatable within the tube, means for disposing the tube in a substantially vertical position, means for introducing carbon dioxide into a first end of the tube which, in use, is located below a second end of the tube, and means for introducing water or the said aqueous suspension of magnesium carbonate at either of the first end or the second end thereof, whereby carbon dioxide is allowed to bubble through the tube and to be intimately contacted with the water or said aqueous suspension of magnesium carbonate.

The apparatus may further comprise means for bottling the magnesium carbonate solution. The means may be or may comprise means for bottling the solution with air, nitrogen or carbon dioxide under a pressure from about 120kPa to about 500kPa.

According to a fifth aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate at a pH, after reaction of the said species with the magnesium carbonate, falling within a range of from about 8,0 to about 8,8;
- controlling the pH of the said solution within the said range until substantially all of the said magnesium carbonate has been converted to dissolved magnesium bicarbonate; and
- bottling the said magnesium bicarbonate solution.

According to a sixth aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate at a pH, after reaction of the said species with the magnesium carbonate, falling within a range of from about 8,0 to about 8,8;
- agitating the suspension so as to keep in suspension a major portion of the magnesium carbonate until substantially all of the said magnesium carbonate has been converted to dissolved magnesium bicarbonate; and
- bottling the said aqueous magnesium bicarbonate solution.

According to a seventh aspect of the present invention, there is provided an apparatus suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:

- means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate;

- means for controlling the pH of the solution between about 7 and about 9 by adjusting the amount of at least one of the said species and the said powdered magnesium carbonate that is contacted with the other; and
 - means for bottling the said solution of magnesium bicarbonate.
- 5 According to an eighth aspect of the present invention, there is provided an apparatus suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:
- means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate;
- 10 - means for keeping in suspension a major portion of said powdered magnesium carbonate until substantially all of the suspended magnesium carbonate has been converted to dissolved magnesium bicarbonate; and
- means for bottling said solution of magnesium bicarbonate.

Brief Description of the Drawings

- 15 A preferred form of the present invention will now be described, by way of example, with reference to the accompanying drawings, wherein:
 Figure 1 is a diagrammatic representation of an apparatus in accordance with the third and fourth aspects of the invention; and
 Figure 2 is a diagrammatic cross-sectional view of a sparger forming part of the apparatus
 20 of Fig 1.

Detailed Description of the Preferred Embodiments

Referring to Figure 1, there is shown an apparatus 10 suitable for preparing an aqueous solution of magnesium bicarbonate. The apparatus 10 comprises means 12 for contacting, with species resulting from the dissolution of carbon dioxide in water, a
 25 suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate.

The means 12 comprises a batch tank 14 of about 27 000 l capacity for containing the aqueous suspension of magnesium carbonate. In a batch process, the tank 14 is preferably large enough to contain sufficient suspension of magnesium carbonate for a desired
 30 production run. In the case of a continuous process, the tank 14 may be of a relatively smaller size, just enough for the contacting step to take place. However, a suitable reactor which may be in the form of a clarifier or other similar piece of equipment, may be provided downstream of the contacting step, to ensure that the reaction between the magnesium carbonate and the said species will run to substantial completion.

The apparatus 10 further comprises means 16 for measuring and controlling the pH of the solution between about 8.0 and about 8.6.

The means 12 for contacting the said species with magnesium carbonate also comprises means 18.1, 18.2 for dissolving carbon dioxide in water or in the said suspension so as to form a solution containing the said species.

The means 18.1, 18.2 for dissolving carbon dioxide comprises a sparger 20.1, 20.2 or other suitable device for breaking up the carbon dioxide into small bubbles. The sparger 20.1, 20.2 may discharge carbon dioxide into and may co-operate with a venturi or similar device located in a pipe through which water may be passed.

As is shown in Figure 2, the sparger 20.1 comprises a porous separation means 22 (as is shown in Figure 2, made of a suitable fabric or porous membrane, in the form of a woman's stocking, is disposed around a tube 24 having a plurality of holes drilled through its sides. The upper end 24.1 of the tube 24 is blanked off, whilst a further tube 26 of smaller cross-section conveys carbon dioxide into the tube 24 through a closure 24.3 covering its bottom end 24.3. The separation means 22 are held tight on the outside of the tube 24 by means of suitable rings or bands 28.

The separation means 22 is capable of separating pressurised carbon dioxide from the suspension or water into which the carbon dioxide is to be dissolved, the pores of the separation means 22 extending from a gas side thereof, which is located on the inside of the tube 24, to a water side thereof, in use, which is located on the outside of the separation means 22. The pores through the separation means are capable of breaking the carbon dioxide up into a plurality of small bubbles, so as to increase the intimacy of contact between the carbon dioxide and the water.

The means for dissolving carbon dioxide comprises, in addition to or as an alternative to the aforementioned sparger means 20.1, 20.2, a tube 30 and a helical baffle 32 locatable within the tube 30, and means 34 for disposing the tube 30 in a substantially vertical position.

The means for dissolving carbon dioxide further comprises means in the form of a carbon dioxide source 36 and a pipe 38 for introducing carbon dioxide into a first end 30.1 of the tube which, in use, is located below a second end 30.2 of the tube 30. The means for dissolving carbon dioxide also comprises means in the form of an external circulating pump 40 for introducing water or the said aqueous suspension of magnesium carbonate at the first end 30.1 of the tube 30, whereby carbon dioxide is allowed to

bubble through the tube 30 and to be intimately contacted with the water or said aqueous suspension of magnesium carbonate.

The means 34 may be a pipe connected to the tank 14 and introducing liquid into the tank 14 through one or more distributors, which may be in the form of pipes with laterally extending holes through which the carbon dioxide enriched suspension or water may be injected into the tank 14 at positions strategically relative to the submersible pumps, so as to maximise the agitation and turbulence in the tank 14.

The means 16 for measuring and controlling may further comprise means (not shown) for respectively adding a caustic or an acidic solution to the contents of the tank 12 when the pH is either too low or too high, or else the control means may be adapted to or may comprise means adapted to reduce or increase the amount of carbon dioxide which is dissolved in the suspension. The means 16 may alternatively or additionally comprise an exhaust system to remove excess carbon dioxide, which tends to lower the pH value of the suspension and solution, from above the liquid inside the tank 14.

The apparatus may further comprise means for bottling the magnesium carbonate solution (not shown) with carbon dioxide under a pressure of from about 120 kPa to about 500 kPa.

Submersible pumps 42 are provided to further increase agitation in the tank 14. They may be replaced by suitable mixers. The submersible pumps and mixers are lowered and controlled inside the tank 14 so that the surface of the suspension or solution is not excessively mixed with the carbon dioxide blanket which forms in layers above the surface of the suspension and solution. This is particularly important when the reaction nears completion and as the volumes of the suspension and solution inside tank 14 decrease during the emptying or bottling processes.

Means 44 are provided for measuring and controlling the temperature of the water or suspension inside the tank 14. The temperature is conveniently controlled around 15°C.

Magnesium carbonate, which may conveniently be in the form of commercially available magnesium carbonate hydroxide pentahydrate $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ is added to the tank 14 through an opening 46 in its top side. The magnesium carbonate may be in powder form or alternatively, it may be in the form of a slurry with water, or else in a concentrated suspension pre-mixed in a mixing tank (not shown).

An outlet 48 for magnesium bicarbonate solution and an inlet 50 for fresh water make-up, are also provided.

Valves 52, 54 are provided so as to be able to inject carbon dioxide either on the suction side of the pump 40 or on its discharge side, or both.

The pressure above the liquid surface in the tank 14 is preferably controlled at a level sufficiently high to ensure that carbon dioxide dissolves at a high enough rate for the reaction between magnesium carbonate and the said species to take place at a rate high enough to ensure that the processing time is reduced to a maximum of a few hours, preferably to a maximum of about 4 to 8 hours, more preferably, to a maximum of 1 to 2 hours. As was mentioned above, the amount of carbon dioxide taking part in the reaction may be controlled, particularly towards the end of the reaction, by removal of excess carbon dioxide by means of the aforementioned exhaust system.

Means (not shown) may be provided for measuring the turbidity of the solution in the tank 14, so as to determine when the solution is ready for bottling.

Example 1: Preparation of Mildly Alkaline Magnesium Bicarbonate Aqueous Solution.

A magnesium bicarbonate solution having a pH value of about pH 8.3 and containing about 125 mg of magnesium cations per litre and 650 mg of bicarbonate anions per litre was prepared in a 27,000 litre tank by reacting magnesium carbonate suspended as a powder in water with carbon dioxide dissolved in the water. The reaction time was 3 hours.

The pH of the contents of the tank was controlled so as to have an end value of 8.3. Initially the pH was higher than 8.3, even as high as about, but it was controlled by controlling the amounts of the magnesium carbonate powder that was added to the tank as well as the amount of carbon dioxide that was dissolved in the water.

The temperature of the contents of the tank was maintained at 15 °C.

The contents of the tank were continuously agitated by means of two submersible pumps suspended in the tank, and by an external pump taking suction from the tank and discharging carbon dioxide enriched suspension back into the tank.

Carbon dioxide was dissolved in the water in the external circulation circuit, either on the suction side of the circulating pump, or, alternatively, on the discharge side, before subjecting the water and carbon dioxide mixture to a helically shaped baffle disposed inside the external tube of the circulation circuit. After reaction of the carbon dioxide with the magnesium carbonate and when the reaction was substantially or finally complete, i.e.

when the turbidity was zero or no more than a slight haze, the specific aqueous solution of magnesium bicarbonate was passed through a 1 micron filter and bottled.

Dated 5 April, 2002

Bertshell Pty Ltd

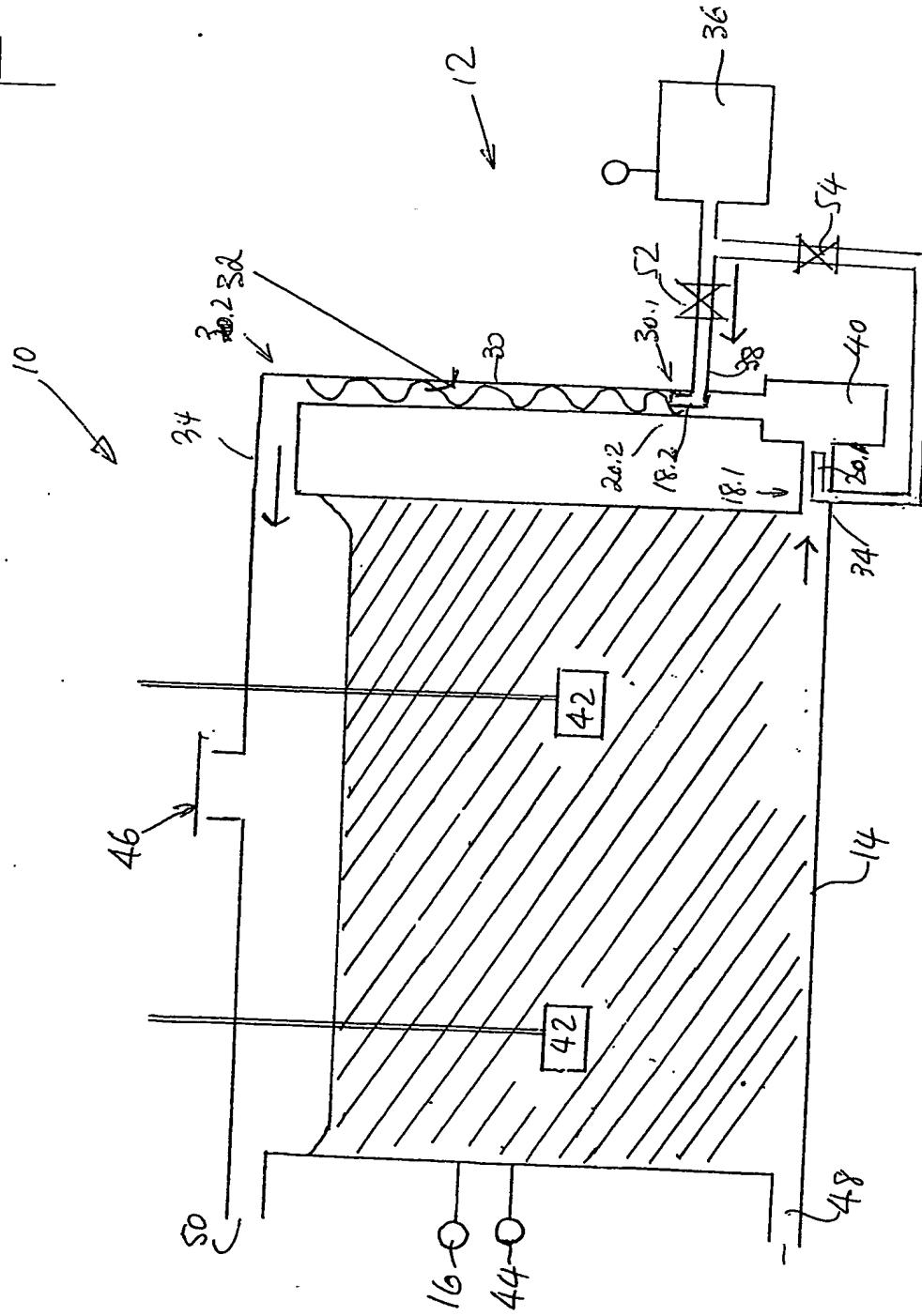
Macquarie Veterinary Supplies Pty Ltd

Patent Attorneys for the Applicants/Nominated Persons

SPRUSON & FERGUSON

1

FIG 1



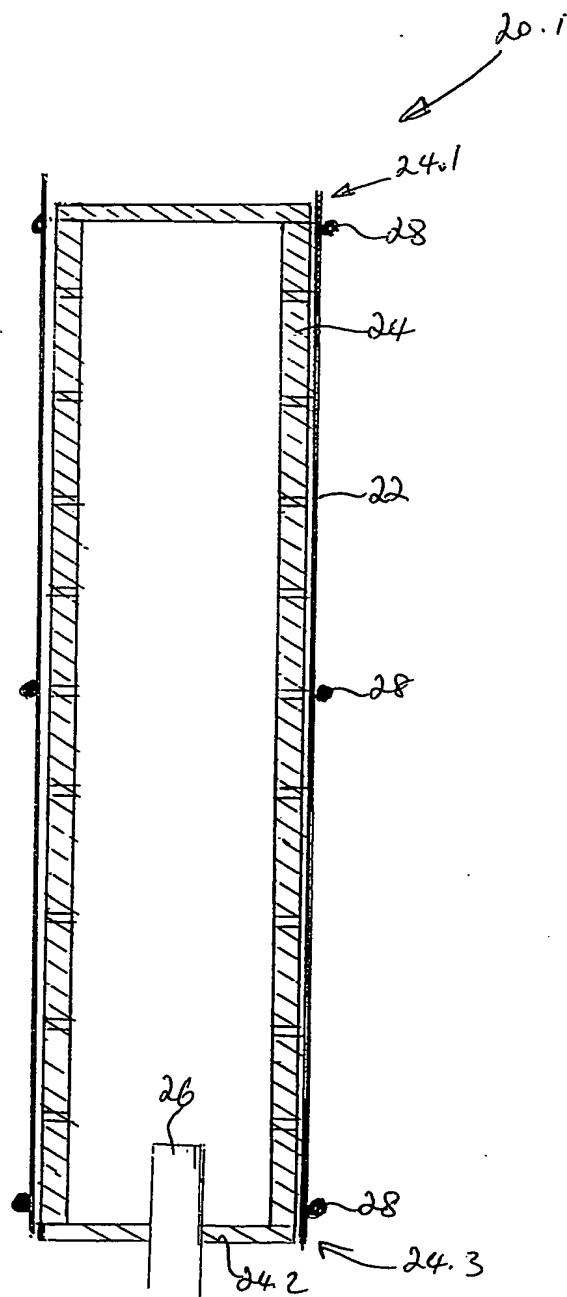


FIG 2